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Short Communication

Evaluating the performance of polypyrrole nanowires on the electrochemical sensing of ammonia in solution

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ABSTRACT

This work encompasses the direct electrodeposition of polypyrrole nanowires onto Au substrates using different electrochemical techniques: normal pulse voltammetry (NPV) and constant potential method with the aim in applying these films for the first time in ammonia sensing in solution. The performance of these nanowire-based sensors are compared and evaluated in terms of: film morphology (analyzed with scanning electron microscopy); their sensitivity towards ammonia; electrochemical and contact angle measurements. For nanowires prepared by NPV, the sensitivity towards ammonia increases with increasing amount of electrodeposited polypyrrole, as expected due to the role of polypyrrole as electrochemical transducer for ammonia oxidation. On the other hand, nanowires prepared potentiostatically displayed an unexpected opposite behavior, attributed to the lower conductivity of longer polypyrrole nanowires obtained through this technique. These results evidenced that the analytical and physico-chemical features of nanostructured sensors can differ greatly from those of their conventional bulky analogous.

1. Introduction

Polypyrrole (PPy) is a conducting polymer often used as electrochemical transducer in sensors and biosensors. Most applications of PPy as sensor comprise gas detection, especially ammonia [1–4]. However, detecting ammonia in solution is environmentally and clinically relevant, because this chemical compound is produced in a large amount by industries to be used as fertilizer and pesticide, and because it is an indicator of kidney disorder or bacterial infection in humans [5,6]. For that reason, many authors have put their efforts on the development of polypyrrole-based sensors for determination of ammonia in solution [7–9]. Detection mechanisms involved in ammonia sensing by polypyrrole, either in gas phase or in solution, have been well elucidated in the literature [1,10], and include reversible and irreversible changes of the electronic properties of polypyrrole, a p-type semiconductor [11], upon treatment with ammonia.

In addition to the application of polypyrrole in sensors, this polymer can be the platform for the development of various biosensors upon immobilization of a desired biological moiety. Examples include the immobilization of enzymes [12–14], DNA [15], and antibodies [16] onto polypyrrole to perform selective detection of chosen analytes. Another interesting feature of polypyrrole and its derivatives is their improved biocompatibility in comparison with bare metallic medical devices [17], turning these materials into excellent choices for a wide range of bioapplications.

Concerning all these possible applications of polypyrrole in sensing and biosensing, the new emerging trend in this area is to benefit from the improved analytical parameters achieved when nanostructured polypyrrole is employed. The synthesis of many different polypyrrole nanostructures has been described in the literature and include: nanopores [18–20] and nanowires [15,21–23], among many others. However, up to date, only a few articles explored the sensing capabilities of polypyrrole nanowires towards ammonia, and only in the gas phase [24–26]. In those articles, the authors employ either the time-consuming procedure of growing polypyrrole nanowires inside a previously obtained aluminum oxide template, or the multi-step method of growing polypyrrole by vapor deposition polymerization onto matrixes of electrospun fibers.

So, in this communication we report the one-step direct electrodeposition (without templates) of polypyrrole nanowires aiming to employ them for the first time as simple and sensitive amperometric sensors for ammonia in solution.

2. Materials and methods

2.1. Electrodeposition of polypyrrole nanowires

Polypyrrole nanowires were electrodeposited over gold electrodes (0.02 cm^2) following two different electrochemical proce-

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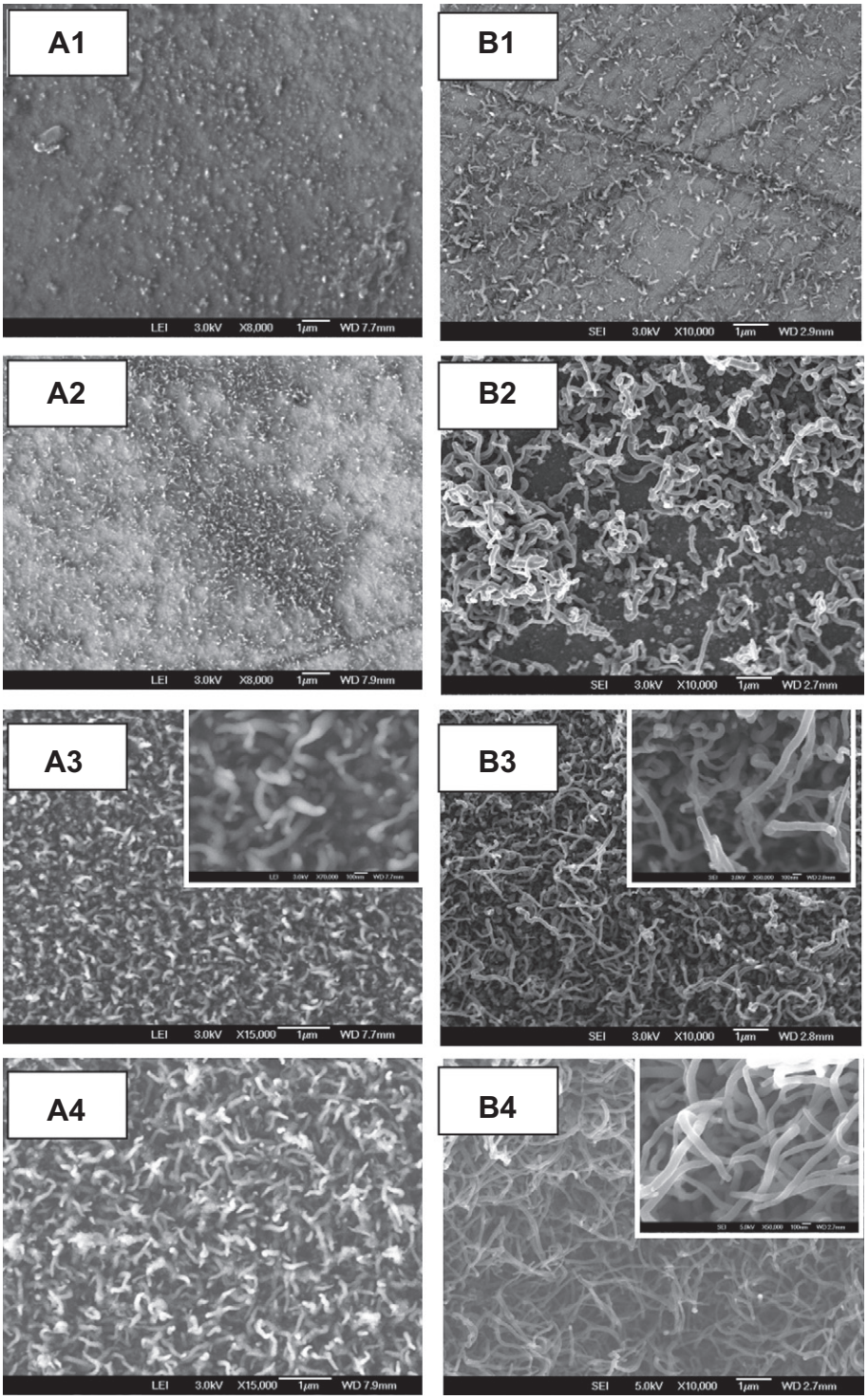

Fig. 1. FESEM images (scale bars = 1 μm) of electrodes containing polypyrrole nanowires prepared according two different procedures: (A) normal pulse voltammetry (A1 = 5 scans; A2 = 10 scans; A3 = 30 scans; A4 = 50 scans) or (B) potentiostatic deposition (B1 = 0.05 C cm^{-2} of deposited polymer; B2 = 0.15 C cm^{-2}; B3 = 0.20 C cm^{-2}; B4 = 0.50 C cm^{-2}). The insets correspond to the respective films displayed in larger magnifications (scale bars = 100 nm).

dures, as described in the next items. In both cases, deposition was carried out from a phosphate buffer solution (0.1 mol L^{-1}, pH 7.0) containing 0.1 mol L^{-1} pyrrole and 0.1 mol L^{-1} $LiClO_4$. All electrochemical experiments were performed in a three electrode conventional cell, which consisted of Au as working electrode, a Pt foil as auxiliary electrode, and Ag/AgCl/saturated KCl as reference.

2.1.1. Normal pulse voltammetry

This procedure consists in applying a sequence of normal pulse voltammetry (NPV) scans to the working electrode [27], and its use on the deposition of polypyrrole nanowires was first demonstrated by Ghanbari and coworkers [15]. The potential ramp of the voltammograms starts in 0.0 V and goes up to 0.8 V in a pulsed manner.

Table 1
Analytical parameters and respective standard deviations of ammonia sensors based on polypyrrole nanowires synthesized electrochemically via normal pulse voltammetry or at constant potential (0.7 V). Results based on three successive measurements on distinct electrodes.

Electrodeposition method	Electrode characteristics given by each preparation method	Sensitivity ($\mu A\ cm^{-2}\ mmol^{-1}\ L$)	Detection limit[a] ($\mu mol\ L^{-1}$)
Normal pulse voltammetry (varying number of NPV scans)	5	–[b]	–
	10	–[b]	–
	30	2.230 ± 0.201	13.96 ± 2.58
	50	6.150 ± 0.302	4.78 ± 0.09
Constant potential (varying charge – in $C\ cm^{-2}$ – of electrodeposited PPy)	0.05	–[b]	–
	0.15	–[b]	–
	0.25	0.360 ± 0.041	11.14 ± 0.85
	0.50	0.120 ± 0.002	8.64 ± 1.40

[a] Calculated according to S/N = 3.
[b] These sensors do not detect ammonia because the amount of PPy present is insufficient to provide an efficient and measureable electrochemical transduction.

The following experimental parameters were employed: potential step = 4.0 mV, pulse width = 0.4 s, pulse period = 1.4 s. Electrodes containing different amounts of electrodeposited polypyrrole were prepared applying from 5 to 50 NPV scans.

2.1.2. Constant potential method

An alternative method to achieve the template-free electrodeposition of polypyrrole nanowires was adapted from the work of Zang and coworkers [22]. Here, a constant potential of 0.7 V vs. $Ag/AgCl/KCl_{sat}$ was applied to the working electrode, until the desired amount of polypyrrole (in terms of the electrical charge, in $C\ cm^{-2}$, generated upon pyrrole oxidation) is electrodeposited over the Au substrate. Electrodes presenting from 0.05 to 0.50 $C\ cm^{-2}$ of polypyrrole nanowires were analyzed in this work.

2.2. Ammonia sensing

After the electrochemical deposition of polypyrrole nanowires, the electrodes were analyzed on a field emission scanning electron microscope (FESEM, JSM-7401F from JEOL), and they were subsequently evaluated as ammonia sensors. For that purpose, ammonia detection was performed amperometrically at 0.35 V in 0.1 mol L^{-1} borate buffer solution (prepared from H_3BO_3) at pH 10.0 (adjusted with NaOH), under constant stirring (using a magnetic mixer). Aliquots of NH_4Cl solution with known concentration were periodically added to the electrolyte to verify sensors responses towards NH_3 (as the pKa of NH_4^+ is 9.24, NH_3 is the predominant species at pH 10.0).

Measurements were performed at 25 ± 1 °C, and they were all repeated at least twice.

3. Results and discussion

3.1. Synthesis and morphological characterization of polypyrrole nanowires

In this work, two different template-free electrochemical procedures were tested for the deposition of polypyrrole nanowires: normal pulse voltammetry (NPV) and constant potential method. The main advantage of employing these methods is that no surface pre-treatment or template must be employed, because in these cases the mechanisms of nanowire growth are based only on the reactants present in the electrolyte and on the potential program applied to the working electrode. The resulting nanowire-containing electrodes will be compared in terms of sensitivities towards ammonia detection.

Concerning the NPV deposition method, the synthesis of nanowires was carried out varying the number of potential scans between 5 and 50. FESEM images in Fig. 1A reveal the increase in both (a) covering of gold substrate by PPy nanowires and (b) diameter of the nanowires with the increase in the number of potential scans applied to the working electrode. Applying 5–10 cycles, only a small amount of polymer is formed over the working electrode, and in these cases it is possible to observe the initial growth of the wires. From 30 to 50 cycles, nanowires length increases from roughly 500 nm in the first case up to 800 nm in the latter (the accurate determination of the length is difficult due to the entanglement of wires).

The main practical advantage of employing a constant potential method instead of NPV to electrodeposit polypyrrole nanowires lies on the fact that the first one allows the direct determination of the amount of polymer (in $C\ cm^{-2}$) formed on the electrode (the area under j vs. t curve provides the charge density of polypyrrole film). This enables the comparison of different sensors directly in function of their amount of polypyrrole. Fig. 1B shows FESEM micrographs of electrodes containing from 0.05 to 0.50 $C\ cm^{-2}$ of polypyrrole nanowires. These images reveal that there is a tendency of increase in substrate covering and nanowires length with increasing charge density of polymer nanowires. Electrodes containing more than 0.15 $C\ cm^{-2}$ of polypyrrole become fully covered, and only nanowires length (and consequently their entanglement) slightly increases.

3.2. Ammonia sensing with polypyrrole nanowires

As has been already discussed in the literature [14], the sensitivity of sensors based on bulk polypyrrole towards NH_3 is directly dependent of the amount of polymer deposited on the electrode, and this is so because polypyrrole acts as an electrochemical transducer for the oxidation of NH_3. In that sense, the possibility of modulating the amount of polypyrrole electrodeposited on the electrode, either by varying the number of NPV scans or the charge density of polypyrrole, is of great importance in this work to compare the analytical parameters of sensors containing different amounts and features (nanowires length) of the polymeric transducer.

The electrodes whose morphologies were displayed in Fig. 1 were employed in ammonia sensing, according to the procedure detailed in the experimental section. The analytical results (sensitivities and detection limits) of these sensors are summarized in Table 1. The films containing polypyrrole nanowires prepared by NPV are very responsive and sensitive to ammonia in solution. Increasing the amount of polypyrrole nanowires (with the increase in number of NPV scans carried out for polymerization) in the sensors causes both the increase in sensitivity and the lowering of detection limit. This behavior confirms the role of polypyrrole as electrochemical transducer in these sensors. On the other hand,

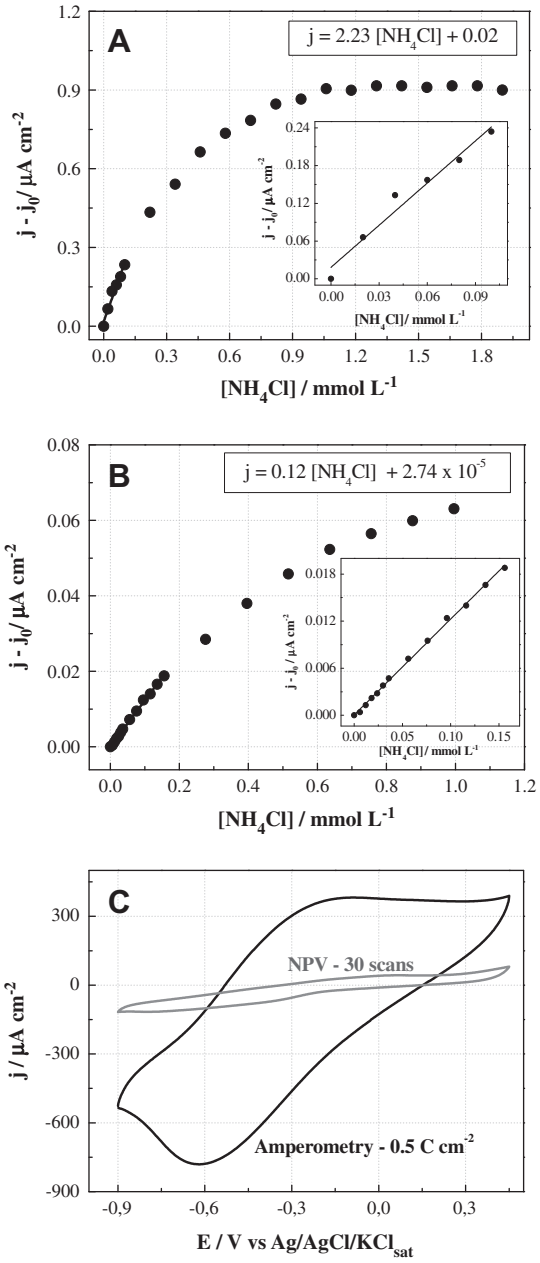

Fig. 2. Analytical curves of sensors containing polypyrrole nanowires: (A) nanowires prepared by normal pulse voltammetry (30 scans = film A3 in Fig. 1); (B) nanowires obtained after potentiostatic deposition (0.50 C cm^{-2} = film B4 in Fig. 1). In both cases, detection was carried out at 0.35 V, in 0.1 mol L^{-1} borate buffer solution (pH 10.0), and at constant stirring. The insets in (A) and (B) show an enlarged view of the initial part of the curves. The current densities given in the *y*-axis are subtracted from the background current, j_0 (in A, j_0 = 0.52 µA cm^{-2}, and in B, j_0 = 0.11 µA cm^{-2}). (C) Cyclic voltammograms (scan rate = 50 mV s^{-1}; electrolyte = 0.1 mol L^{-1} borate buffer solution, pH 10.0) of electrodes described in (A) and (B).

observing the results concerning the sensors containing polypyrrole nanowires prepared potentiostatically, an unexpected trend is depicted in Table 1. In this case, as the charge density of electrodeposited polypyrrole goes from 0.25 to 0.50 C cm^{-2} the sensitivity towards ammonia decreases. This is exactly the opposite of what was expected, considering the role of polypyrrole as transducer in these sensors. This leads to the investigation of other issues that could be causing this odd behavior on sensors containing polypyrrole nanowires potentiostatically electrodeposited, as it will be discussed later.

Another important feature depicted from Table 1 is that the comparison between sensitivities of sensors having polypyrrole nanowires synthesized by NPV and constant potential method shows that these latter ones provide sensitivities around one order of magnitude smaller than the ones obtained via NPV. To exemplify this, Fig. 2A and B displays the analytical curves for sensors containing polypyrrole nanowires prepared by 30 scans of NPV and at constant potential (0.5 C cm^{-2}), respectively. The sensitivity values calculated from the slope of these curves are respectively 2.23 (NPV 30 scans) and 0.12 µA cm^{-2} $mmol^{-1}$ L (constant potential deposition; 0.50 C cm^{-2}). The saturation of the response observed at higher ammonia concentrations are attributed to irreversible interactions between ammonia and polypyrrole, causing changes in the electronic properties of the polymer [28,29]. Interestingly, the cyclic voltammograms of those two electrodes (Fig. 2C) in borate buffer solution (0.1 mol L^{-1}, pH 10.0) reveal that the charge of polypyrrole nanowires present in the sensor prepared at constant potential is much larger than the one prepared by NPV, given the larger area inside the curve in the first case. This corroborates the SEM images of those films (Fig. 1 B4 – NPV 30 scans, and A3 – potentiostatic deposition of 0.5 C cm^{-2}), in which one can observe that the amount of polymer in the film containing nanowires obtained potentiostatically is indeed larger.

The fact that the sensor prepared at constant potential (0.5 C cm^{-2}) contains a larger amount of polypyrrole nanowires but displays the lower sensitivity was first attributed to a possible worse wettability of this film, in comparison with the sensor prepared by NPV 30 scans, since the first possesses a greater entanglement of the wires (as a consequence of longer wire lengths), eventually causing the entrapment of air inside the film. However, contact angle measurements revealed that the wettability of both films is practically the same (potentiostatically deposited 0.5 C cm^{-2} = 34.5° ± 2.9°; NPV 30 scans = 32.1° ± 1.6°).

Given the results discussed here, and after excluding a possible hydrophobic effect, we get to the conclusion that in the case of ammonia sensors based on polypyrrole nanowires, not only the amount of polypyrrole present on the sensor has an effect on the sensitivity (as it is the case for bulk polypyrrole sensors), but also the length of the nanowires accounts for an important contribution on the performance of these nanostructured films as ammonia sensors (since their diameter are approximately the same). The effect of increasing length on nanowires conductance has been already reported in the literature [30]. In this reference, the authors show that the conductance *G* of a metal–molecular wire–metal junction follows a $G = G_0 e^{-\gamma L}$ law with *L* (*L* = wire length and γ = decay constant). Employing density functional theory combined with non-equilibrium Green's function method, Peng and coworkers [31] have determined that oligopyrrole follows that exponential decay law with $\gamma = 0.257$ Å^{-1}. In short, longer nanowires are less conductive than shorter ones, and this will have an immediate effect on the sensing abilities of the nanowire film. For example, the potential on the top of the wire is not the same as the one in its base, due to the resistivity of longer wires. So, ammonia detection would be more favorable only in the initial part of the nanowire (close to its base), where the diffusion of analyte faces a steric hindrance due to the entanglement of the long wires. In that sense, this would not be a problem in the case of shorter nanowires. This result explains: (a) the reduction in sensitivity when the charge density of polypyrrole goes from 0.25 to 0.50 C cm^{-2}, and (b) the lower sensitivities of sensors containing polypyrrole nanowires prepared potentiostatically, in comparison with NPV. As can be seen in the magnified views of the nanowire films (displayed as insets in Fig. 1 – A3 and B4), the length of nanowires prepared at constant potential (0.25 or 0.50 C cm^{-2}) is much larger than those obtained by NPV (30 or 50 scans), corroborating our theory.

These results show a clear evidence that the physico-chemical and analytical behavior of nanostructured polypyrrole sensors can differ greatly from that of their bulky analogous due to the unique properties which are intrinsic to nanostructured platforms.

4. Conclusions

Polypyrrole nanowires were successfully employed for ammonia sensing in solution for the first time. The performance of these materials as ammonia sensors relies basically on a compromise between the amount of polypyrrole electrodeposited onto the base electrode (Au) and the length of the nanowires. Nanowires synthesized by normal pulse voltammetry are more sensitive to ammonia than those synthesized by constant potential method because in the latter case, and using the conditions described in this work, longer and thus less conductive nanowires are formed.

This work envisions the possibility of applying these nanowire films as platforms for the development of biosensors for the indirect detection of urea, via ammonia (upon immobilization of the enzyme urease) [32].

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